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(54) AQUEOUS MIXTURES OF SPECTRALLY SENSITIZING DYES FOR PHOTOGRAPHIC EMULSIONS

**WÄSSRIGE FARBSTOFFSUSPENSIONEN ZUR SPEKTRALEN SENSIBILISIERUNG
PHOTOGRAPHISCHER EMULSIONEN**

**MELANGES AQUEUX DE COLORANTS DE SENSIBILISATION SPECTRALE POUR EMULSIONS
PHOTOGRAPHIQUES**

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(56) References cited:
US-A- 4 006 025 **US-A- 4 683 193**

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Description**FIELD OF THE INVENTION**

5 This invention relates to a process for preparing concentrated dye-water compositions for the spectral sensitization of photographic emulsions.

BACKGROUND OF THE INVENTION

10 Dyes for spectrally sensitizing silver halide emulsions are known to be substantially insoluble in water for all practical purposes. Accordingly, such dyes, as well as other photographic additives which are capable of being adsorbed on the grain surfaces of silver salts, have been added to photographic silver halide emulsions in the form of solutions in suitable water miscible solvents such as methyl alcohol or dimethylformamide.

However, spectrally sensitizing dyes are difficult to dissolve in the usual solvents.

15 Consequently, large quantities of solvent are often needed for satisfactory dissolution of such additives. This presents a significant problem since the presence of residual solvent generally causes diffusion and migration of spectrally sensitizing dyes in the emulsion. Further, even minute residues of solvent promote recrystallization processes in the photographic layer which, in turn, adversely affect not only the dyes and other additives introduced using solvent but other additives in the emulsion as well. Moreover, if residues of polar organic solvents miscible with water remain in a silver halide emulsion, particularly a silver-rich emulsion having a high silver packing density, the residual solvent considerably reduces the stability of the casting emulsion which in turn causes a reduced stability during processing including phase separation between hydrophilic and hydrophobic phases, agglomeration, and coalescence as well as flocculation before casting.

25 Additives which need not be held on the surface of silver halide crystals by adsorption after their introduction into a photographic emulsion have long been incorporated into silver halide emulsions in the form of dispersions. For that purpose, the additive is usually dissolved in a suitable solvent, which is generally immiscible with water, in the presence of an oil former and wetting agent, and then emulsified into an aqueous gelatin solution. The low boiling solvent generally used for this purpose is subsequently removed from the emulsion and the resulting dispersion is added to the photographic silver halide emulsion.

30 Unfortunately, the complete removal of the solvent from the resulting dispersion is difficult to achieve, even when low boiling solvents are employed, and particularly when polar solvents are employed. Polar solvents, in particular polar protic solvents, can be removed from gelatin dispersions only by heating, a process which adversely effects the stability of the sensitizing dye molecule. Alternatively, the use of a vacuum to remove the solvent often causes considerable foaming.

35 One method for obviating the harmful effects of using water miscible or immiscible organic solvents to incorporate substantially insoluble additives into silver halide emulsions and dispersions as described in British Patent 1,570,362 is to sand mill such additives in water to a particle size of less than 1 micron in the presence of a surfactant which gives rise to a surface tension of not less than 38 dynes/cm in water when used in a quantity of 1 g/l.

40 A similar process is disclosed in U.S. Patent 4,006,025 which teaches milling or homogenizing at an elevated temperature in the presence of a surfactant in which the sensitizing dye is at least partially soluble. The process is complicated and the use of surfactant increases finish time.

The process described in U.S. Patent 4,474,872 also requires milling but teaches that the use of a surfactant can be eliminated, but only if the dye is mechanically ground to a fine grain size (1 micron or less). Very elevated temperatures (60°-80° C) are employed for preparing the dispersion, and processing conditions such as pH are strictly controlled. Such a process merely eliminates one problem while introducing a multiplicity of others.

45 The US-A-4,683,193 discloses a process for producing a spectrally sensitized silver halide photographic emulsion, comprising adding a substantially water-insoluble spectral sensitizing dye in an aqueous carrier to an emulsion before completion of the formation of silver halide grains without using an organic solvent.

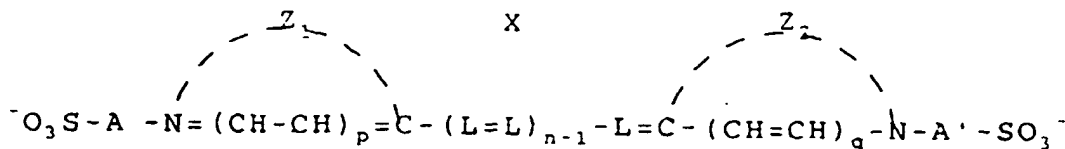
SUMMARY OF THE INVENTION

50 A process for preparing concentrated dye-water compositions for spectrally sensitizing photographic emulsions in the absence of a solvent or surfactant which comprises adding a sensitizing dye having a solubility in water of at least 0.005 weight percent to water or a water-polymer medium with agitation at a temperature of from 20 to 50°C at a concentration of dye which exceeds that amount which is soluble in the water or water-polymer medium at the preparation, usage or storage temperatures, and continuing agitation for at least 30 minutes, preferably up to 5 hours.

55 The process of the invention is simple, versatile and forgiving. It does not require the use of solvents, surfactants, milling of the dye to vary starting grain sizes, use of highly elevated temperatures or pH control.

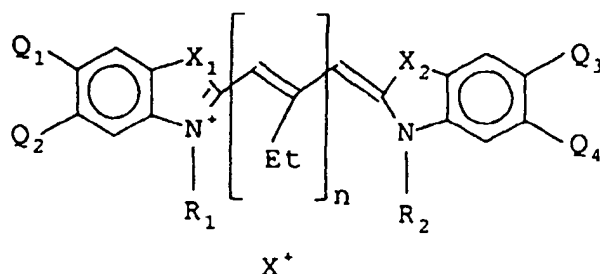
The concentration of dye employed in the process generally exceeds that amount of dye which is soluble in the dispersion medium at the preparation, usage, or storage temperatures. Preferably, amounts ranging from 0.5 to 5 weight percent of dye based on the total weight of the mixture are employed.

Cyanine dyes which have a solubility of at least 0.005% by weight in water are preferably used in the process of the invention. Preferred dyes have the formula



wherein Z_1 and Z_2 each independently represents the atoms necessary to complete a substituted or unsubstituted heterocyclic nucleus, each L independently represents a substituted or unsubstituted methine group, n is a positive integer of from 1 to 4, p and q each independently represents 0 or 1, X represents a cation needed to balance the charge of the molecule, and A and A' each independently represents a divalent alkyl or substituted alkyl linking group.

Even more preferred are dyes having the formula



wherein n is 0 or 1; X_1 and X_2 each independently represents oxygen or sulfur; Q_1 , Q_2 , Q_3 and Q_4 each independently represents halogen, alkyl, alkoxy or may contain the atoms necessary to form a beta or linear naphtho-fused ring; R_1 and R_2 each independently represent a sulfoalkyl or substituted sulfoalkyl group; and X^+ is a cation such as sodium, hydrogen, triethylammonium or ethyl pyridinium.

DETAILED DESCRIPTION OF THE INVENTION

Although the process of the invention provides concentrated sensitizing dye-water compositions that are homogeneous, solvent-free and dispersant-free, such compositions are nevertheless resistant to settling. If some settling does occur, slight agitation or mixing renders the composition homogeneous once again.

Generally, a solid sensitizing dye powder that is somewhat soluble in water is mixed into an "aqueous medium", which term includes a polymer-containing aqueous medium (water-polymer medium), preferably containing gelatin, at a concentration of dye greater than that which will dissolve in the medium at the temperature, pressure, or other conditions of processing, storage, or use of the composition. Amounts ranging from 0.5 to 5 weight percent based on the total weight of the components of the composition are preferred. Because the process can be carried out in the absence of either solvent or surfactant, it is simpler, faster, more forgiving, and more flexible than prior processes.

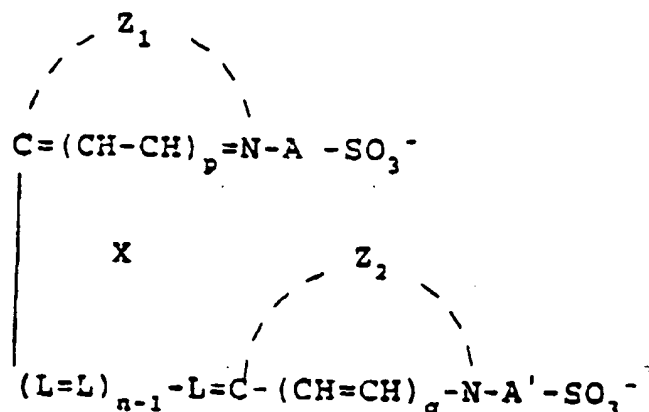
Preferably, the medium to which the dye is added is heated to a preparation temperature ranging from 20° to 50° C and maintained at that temperature throughout dye addition and mixing. When gelatin is employed, it is preferred that a temperature greater than 40° C is used although lower temperatures can be used with other polymers. The process is also flexible in that one temperature can be used during addition while a different temperature is used during mixing.

Mixing or agitation is continued after the addition of the dye is complete and until little evidence of the particles of the original dye powder can be observed. This generally requires from 30 minutes to 5 hours.

The composition can be mixed or agitated by any suitable means using any suitable device including magnetically driven stirring bars of various shapes and motor driven shaft stirrers of the propeller or Cowles type. A formula provided

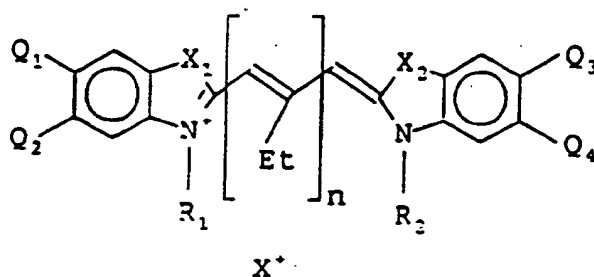
by J. Y. Oldshue in "Fluid Mixing Technology", McGraw-Hill, New York, 1983, p. 83, can be used to calculate the preferred amount of agitation to be used in which where $p/kg = (\text{Diameter})^5 \times (\text{RPM})^3 / \text{Batch size}$ in which Diameter = diameter of Cowles or other blade in inches and Batch size = kg. Best results in terms of minimizing the number of undispersed dye particles can be obtained when $p/kg > 50 \times 10^9$.

The process of the invention can be employed using spectrally sensitizing dyes, particularly spectrally sensitizing cyanine dyes, having a solubility in water of at least 0.005% by weight of the dye in water despite the absence of solvents, dispersants, surfactants or wetting agents. Preferred dyes have the formula



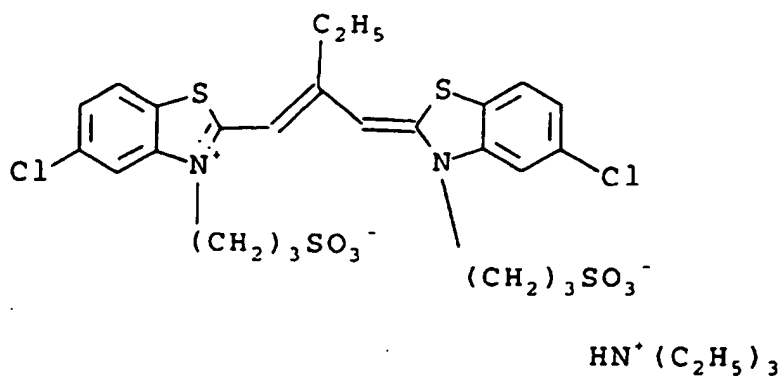
wherein Z_1 and Z_2 each independently represents the atoms necessary to complete a substituted or unsubstituted heterocyclic nucleus, each L independently represents a substituted or unsubstituted methine group, n is a positive integer of from 1 to 4, p and q each independently represents 0 or 1, X represents any suitable cation which will balance the charge of the molecule, and A and A' each independently represents a divalent alkyl or substituted alkyl linking group.

Even more preferred are dyes having the formula

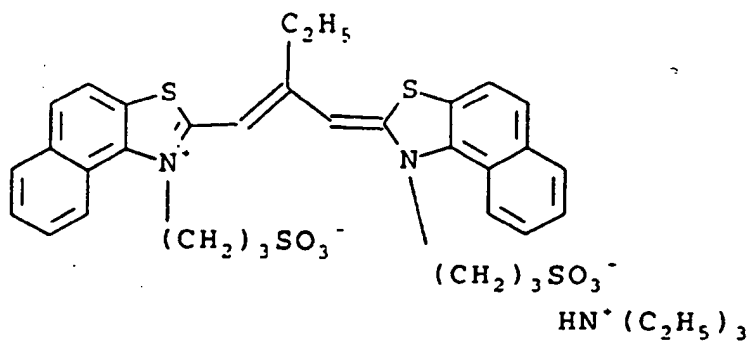


wherein n is 0 or 1; X_1 and X_2 each independently represents oxygen or sulfur; Q_1 , Q_2 , Q_3 and Q_4 each independently represents halogen, alkyl, alkoxy or may contain the atoms necessary to form a beta or linear naphtho-fused ring; R_1 and R_2 each independently represent a sulfoalkyl or substituted sulfoalkyl group; and X^+ is a cation such as sodium, hydrogen, triethylammonium or ethyl pyridinium.

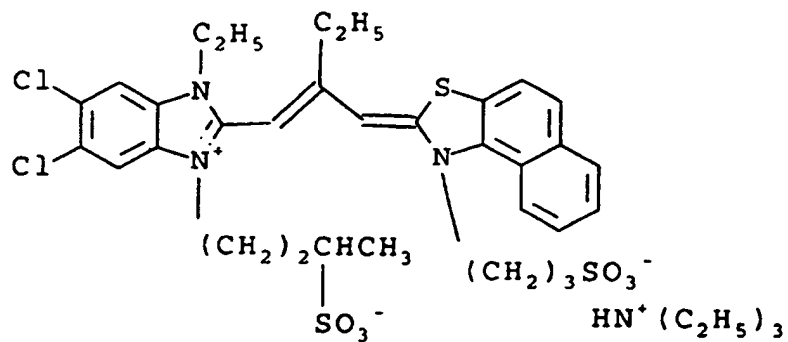
Most preferred to be used in the practice of this invention include structures I through XII.



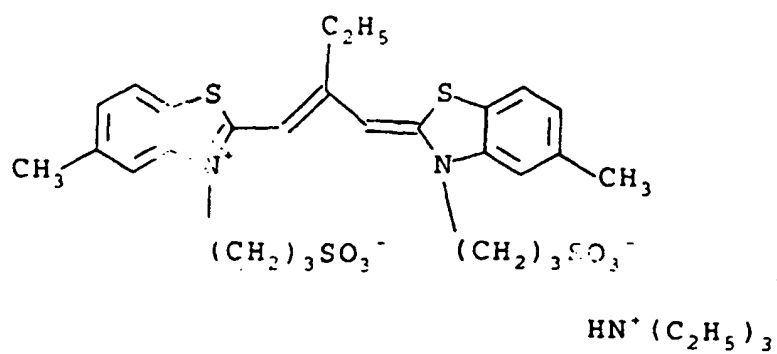
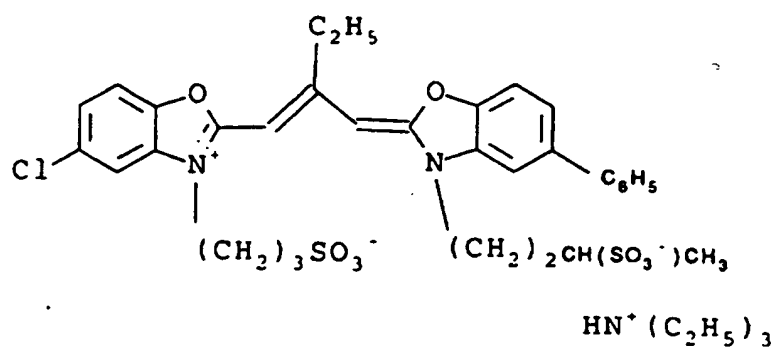
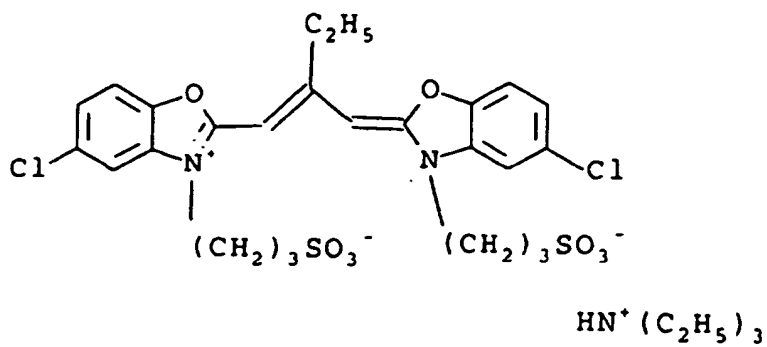
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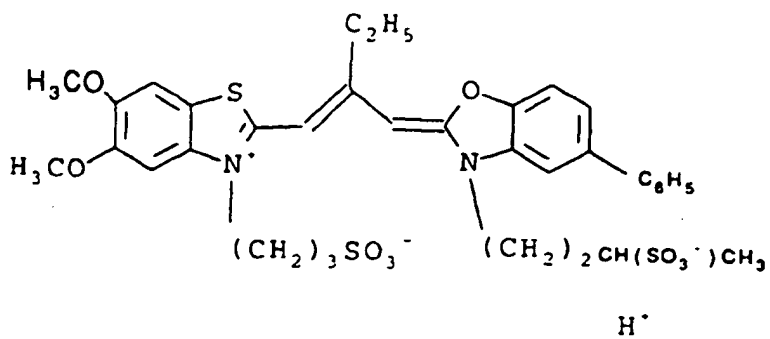


II

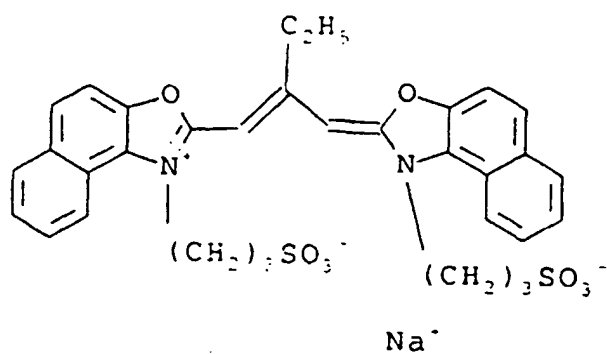


III

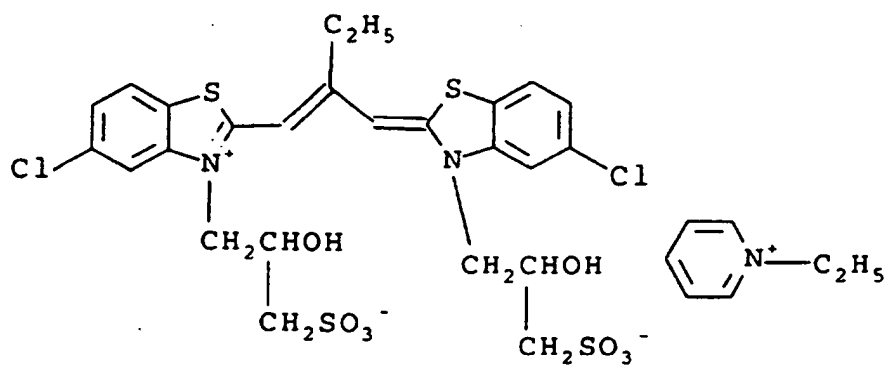




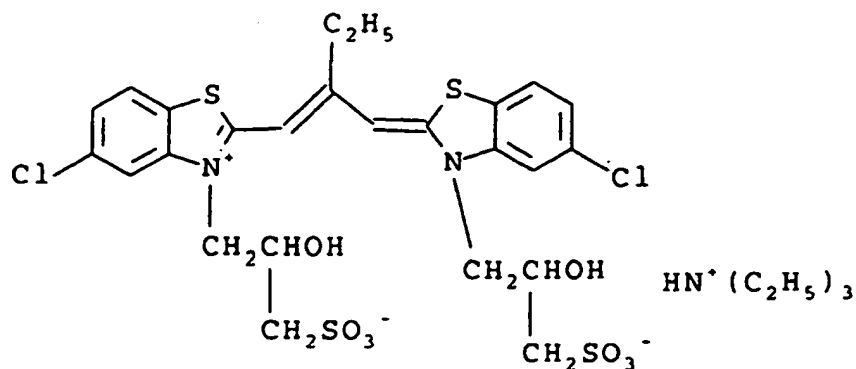
VII



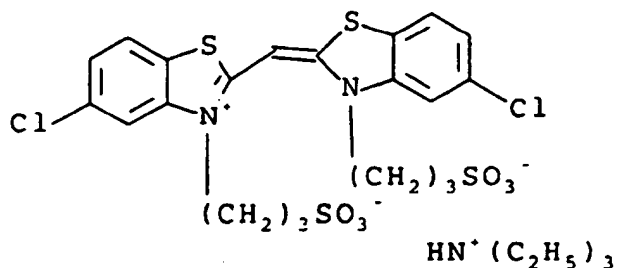
VIII



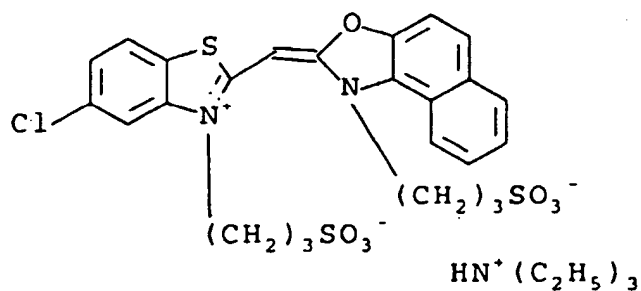
IX



X



XI



XII

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The solvent-free, dispersant-free, dye-water compositions prepared by the process of the invention and containing from 0.5 to 5 weight percent of the dyes defined herein are resistant to settling. Similar compositions prepared by prior methods or containing other dyes require either a solvent or surfactant to provide similar results or else complicated and difficult preparatory methods.

Concentrated sensitizing dye-water compositions for the spectral sensitization of photographic emulsions can be prepared by any suitable method. However, in accordance with the invention, the concentrated dye-water compositions are preferably prepared by first mixing gelatin with water and then heating to prepare an initial gelatin solution. The

gel solution is heated and stirred or mixed or otherwise agitated while a sensitizing dye of the invention is introduced, preferably in the form of a powder slowly and uniformly over the surface of the mixture being stirred. When the addition of the sensitizing dye is completed, stirring is continued for a period of time, generally ranging from 30 minutes to 5 hours or longer as desired, to produce the concentrated dye-water composition of the invention.

More specifically, a dispersion of a salt of a sensitizing dye is in accordance with the invention prepared in a 24.75 cm high stainless steel can having a diameter of about 20 cm into which was introduced about 300 g of dry, deionized, bone gelatin and about 4675 g of distilled water. The mixture was placed in a refrigerator overnight in order to allow the gelatin to swell. The resulting gel-water mixture was then melted and maintained at a temperature of about 50° C until the gelatin dissolves.

While maintaining the temperature at 50° C, a 10 cm Cowles-type stirrer driven by an electric motor was introduced with the blade of the stirrer positioned in the center of the can parallel to and about 7.6 cm from the bottom of the can. Stirring speed is maintained at about 500 rpm while adding about 25 g of a powder of structure IX slowly and uniformly over the surface of the stirred mixture near the vortex and over a time period of about two minutes. The powder is prepared by grinding the dye using a mortar and pestle until the dye passes through a sieve having 1 mm openings.

The blade of the stirrer is then lowered to about 5 cm from the bottom of the can and the rpm's are increased to about 660. Stirring is continued for about one hour. The final dye dispersion contains about 0.5% by weight of dye and about 6% by weight of gelatin based on the weight of the entire dispersion.

The dye compositions prepared according to the invention can also contain a polymeric binder or protective colloid which can be used in the photographic emulsion layers of intermediate layers of a photographic light-sensitive material. Gelatin is advantageously used although other hydrophilic colloids can be used alone or together with gelatin. Either lime processed or acid processed, deionized gelatin can be used.

Any suitable silver halide such as silver bromide, silver iodobromide, silver chlorobromide or silver chloride can be used in the photographic emulsion layer of the photographic light-sensitive material sensitized in accordance with the invention. Particular kinds of silver halide particles and photographic emulsions as described in U.S. Patent 4,741,995, can be employed.

The photographic emulsion can be prepared by any suitable method including an acid process, a neutral process or an ammonia process using a controlled jet process to obtain regular, nearly uniform grain size silver halide crystals which can be ripened in the presence of cadmium salts, zinc salts, lead salts, thallium salts, iridium salts or its complex salts, rhodium salts or its complex salts, iron salts or its complex salts.

Silver halide emulsions are usually chemically sensitized, for example by sulfur sensitization using active gelatin or compounds such as thiosulfates, thioureas, mercapto compounds and rhodanines containing sulfur capable of reacting with silver; a reduction sensitization process using reducing substances such as stannous salts, amines, hydrazine derivatives, formamidesulfonic acid and silane compounds a noble metal sensitization process using noble metal compounds such as complex salts of the Group VIII metals of the Periodic Table including platinum, iridium and palladium as well as gold complex salts; alone or in combination with each other.

The photographic emulsion can include various compounds for preventing fog formation or stabilizing photographic characteristics during production, storage, or processing. For example, antifoggants or stabilizers include azoles such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, mercaptotetrazoles particularly 1-phenyl-5-mercaptotetrazole; mercaptopyrimidines, mercaptotriazines, thioketo compounds such as oxazolinethione, azaindenes such as triazaindenes, tetraazaindenes particularly 4-hydroxy substituted 1,3,3a,7 tetraazaindenes, pentaazaindenes, benzenethiosulfonic acids, benzenesulfonic acids and benzenesulfonic amides.

Various surface active agents can be incorporated into the photographic emulsion or other hydrophilic colloid layers of the photographic light-sensitive materials sensitized in accordance with the invention as coating aids, to prevent charging, improve slip properties, accelerate emulsification and dispersion, prevent adhesion, improve photographic characteristics such as accelerating development, high contrast and sensitization.

The photographic emulsion layer can also contain compounds such as polyalkylene oxide or derivatives thereof such as ether, ester, amine derivatives, thioether compounds, thiomorpholines, quaternary ammonium salt compounds, urethane derivatives, urea derivatives, imidazole derivatives, and 3-pyrazolidones to increase sensitivity or contrast or accelerate development.

Water insoluble or only sparingly soluble synthetic polymer dispersions can be incorporated into the photographic emulsion layer or other hydrophilic colloid layer to improve e.g. dimensional stability. Some synthetic polymers which can be used include homo or copolymers of alkyl acrylate or methacrylate, alkoxyalkyl acrylate or methacrylate, glycidyl acrylate or methacrylate, acrylamide or methacrylamide, vinyl esters such as vinyl acetate, acrylonitrile, olefins or styrene and copolymers thereof with acrylic acid, methacrylic acid, alpha, beta-unsaturated dicarboxylic acid, hydroxy-alkyl acrylate or methacrylate, sulfoalkyl acrylate or methacrylate and styrenesulfonic acid.

In addition to the concentrated dye-water composition of the invention for spectrally sensitizing photographic emul-

sions prior to coating on a support, other sensitizing dyes can be used which do not in themselves give rise to spectral sensitization but provide a supersensitizing effect such as, for example, aminostyryl compounds substituted with a nitrogen-containing heterocyclic group including those described in U.S. Patents 2,933,390 and 3,635,721, aromatic organic acid-formaldehyde condensates such as those described in U.S. Patent 3,743,510 cadmium salts and azainden compounds.

The concentrated dye-water sensitizing compositions prepared according to the invention can be used in multilayer multicolor photographic materials containing layers sensitive to at least two different spectral wavelength ranges on a support. A multilayer natural color photographic material generally possesses at least one red-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer, and at least one blue-sensitive silver halide emulsion layer on a support. The order of the layers can be varied as desired. Ordinarily, a cyan forming coupler is present in the red-sensitive emulsion layer, a magenta forming coupler is present in the green-sensitive emulsion layer, and a yellow forming coupler is present in the blue-sensitive emulsion layer, respectively. Different combinations can be employed as desired.

Any suitable dye-forming couplers, that is, compounds capable of forming color upon oxidative coupling with aromatic primary amine developing agents such as phenylene-diamine derivatives or aminophenol derivatives during color development processing, can be incorporated into the same or different photographic silver halide emulsion layer as desired. Examples of some such couplers include magenta couplers such as 5-pyrazolone coupler, cyanoacetyl-coumarone couplers and open chain acylacetone couplers; yellow couplers such as acylacetamide couplers including benzoylacetonilides pivaloylacetonilides; cyan couplers such as naphthol couplers and phenol couplers.

Preferably, nondiffusible couplers containing a hydrophobic group or ballast group within the molecule or polymeric coupler is used. They may be either 4-equivalent or 2-equivalent with respect to silver ions. Colored couplers capable of exerting color correction effects or couplers capable of releasing development inhibitors during the course of development or DIR couplers, can also be used. Two or more couplers can be employed.

The photographic material can contain inorganic or organic hardeners in the emulsion layer or other hydrophilic colloid layer thereof. For example, chromium salts such as chromium alum or chromium acetate; aldehydes such as formaldehyde, glyoxal or glutaraldehyde; N-methylol compounds such as dimethylolurea, methyloldimethylhydantoin and the like; dioxane derivatives such as 2,3-dihydroxydioxane; active vinyl compounds such as 1,3,5-triacryloylhexahydro-s-triazine; mucohalogenic acids such as mucochloric acid or mucophenoxy-chloric acid can be used, either alone or in combination.

When dyes, e.g. ultraviolet light absorbing agents, are incorporated in the hydrophilic colloid layers of a photographic light-sensitive material, they may be mordanted with cationic polymers. The photographic light-sensitive material can also contain hydroquinone derivatives, aminophenol derivatives, gallic acid derivatives and/or ascorbic acid derivatives as color fog preventing agents.

Dyes which can be incorporated into the hydrophilic colloid layers of a photographic light sensitive material of the invention include benzotriazole compounds substituted with aryl groups, and 4-thiazolidone, benzophenone, cinnamic acid ester, butadiene and/or benzoxazole.

Ultraviolet light absorbing couplers such as alpha naphthol type cyan dye forming couplers and ultraviolet light absorbing polymers can also be used. Such ultraviolet light absorbing agents can also be mordanted in a specific layer, if desired.

Photographic light sensitive elements prepared using emulsions spectrally sensitized with dye-water compositions prepared according to the invention may contain water soluble dyes in the hydrophilic colloid layers as a filter dye or for other purposes such as irradiation prevention and the like. Some such suitable dyes include for example oxonol, hemioxonol, styryl, merocyanine, cyanine or azo dyes. Oxonol, hemioxonol, and merocyanine dyes are particularly useful.

Any suitable color fading prevention agents can also be used as well as color image stabilizers, either alone or in combination with each other. Some suitable color fading prevention agents include hydroquinone derivatives, gallic acid derivatives, p-oxyphenol derivatives and/or bisphenols.

Silver halide photographic emulsions sensitized in accordance with the invention can also contain various other additives used for photography including any suitable hardeners, surfactants, fluorescent whiteners, physical property modifiers such as humectants or water dispersants; condensates of phenols and formalin.

Silver halide emulsions sensitized in accordance with the invention can be coated on any suitable support and dried to prepare a light sensitive silver halide photographic element. Some suitable supports include paper, glass, cellulose acetate, cellulose nitrate, polyester, polyamide, polystyrene or laminated products of two or more substrates such as laminated products of paper and a polyolefin such as polyethylene or polypropylene,

The support may be subjected to various surface modification treatments for improving adhesion to the silver halide emulsion such as subbing or electron impact treatment.

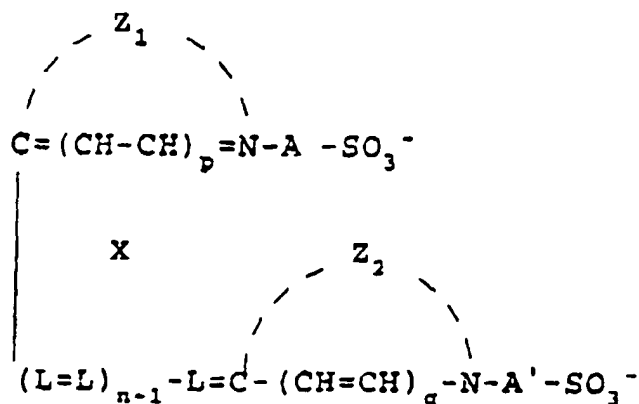
Coating and drying of the silver halide photographic emulsion on the support may be carried out conventionally by dip coating, roller coating, multislide hopper coating or curtain flow coating followed by drying.

By combining various photographic layers from layers sensitized to other wavelengths such as green sensitive and red sensitive silver halide emulsion layers, intermediate layers, protective layers, filter layers, antihalation layers, backing layers and others, a light sensitive color photographic element can be formed. In such a case, each light sensitive emulsion layer can comprise two emulsion layers with different sensitivities.

Although the invention has been described in considerable detail in the foregoing it is to be understood that such detail is solely for the purpose of illustration and that variations can be made by those skilled in the art.

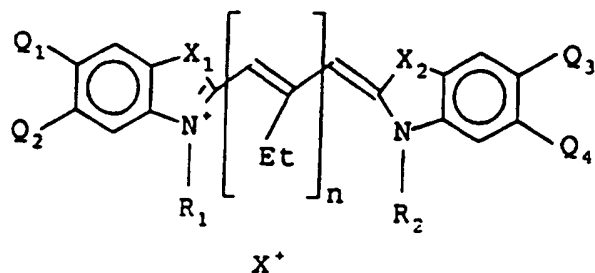
Claims

1. A process for preparing concentrated dye-water compositions for spectrally sensitizing photographic emulsions in the absence of a solvent or surfactant which comprises adding a sensitizing dye having a solubility in water of at least 0.005 weight percent to water or a water-polymer medium with agitation at a temperature of from 20 to 50°C at a concentration of dye which exceeds that amount which is soluble in the water or water-polymer medium at the preparation, usage or storage temperatures, and continuing agitation for at least 30 minutes, preferably up to 5 hours.
2. The process of claim 1 wherein from 0.5 to 5 weight percent of dye based on the total weight of the mixture is added to the water or water-polymer medium.
3. The process of claim 2 wherein agitation (p/kg) greater than 50×10^9 is employed.
4. The process of claim 2 or 3 wherein the dye is a cyanine spectrally sensitizing dye.
5. The process of claim 4 wherein the cyanine dye has the formula



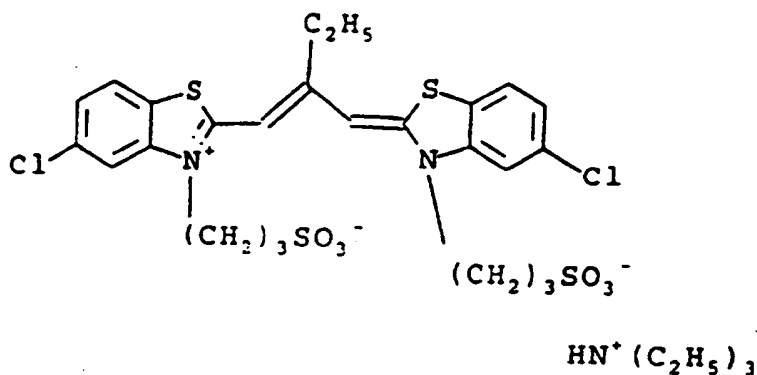
wherein Z_1 and Z_2 each independently represents the atoms necessary to complete a substituted or unsubstituted heterocyclic nucleus, each L independently represents a substituted or unsubstituted methine group, n is a positive integer of from 1 to 4, p and q each independently represents 0 or 1, X represents a cation needed to balance the charge of the molecule, and A and A' each independently represents a divalent alkyl or substituted alkyl linking group.

6. The process of claim 5 wherein the dye has the formula

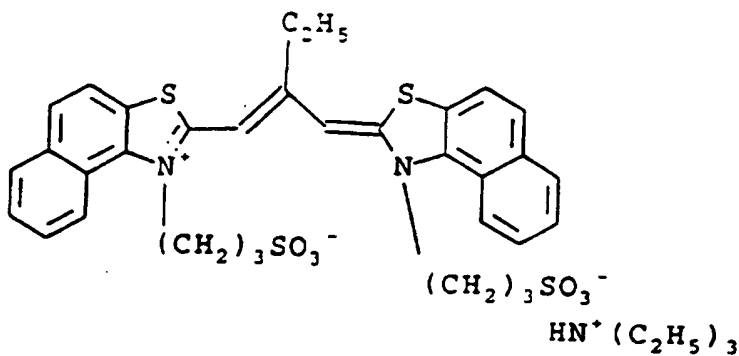


wherein n is 0 or 1; X_1 and X_2 each independently represents oxygen or sulfur; Q_1 , Q_2 , Q_3 and Q_4 each independently represents halogen, alkyl, alkoxy or may contain the atoms necessary to form a beta or linear naphtho-fused ring; R_1 and R_2 each independently represent a sulfoalkyl or substituted sulfoalkyl group; and X^+ is a cation such as sodium, hydrogen, triethylammonium or ethyl pyridinium.

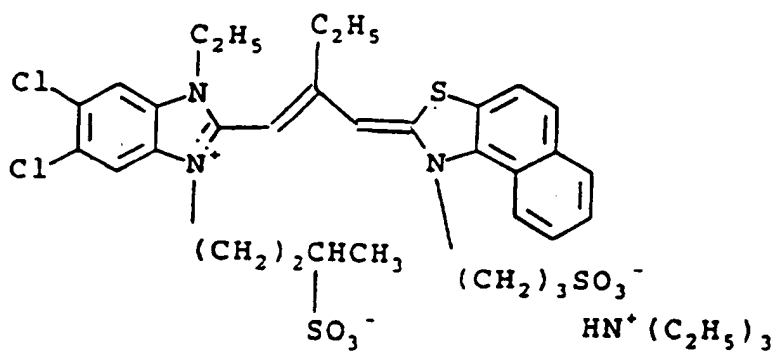
7. The process of claim 6 wherein the dye has the structure



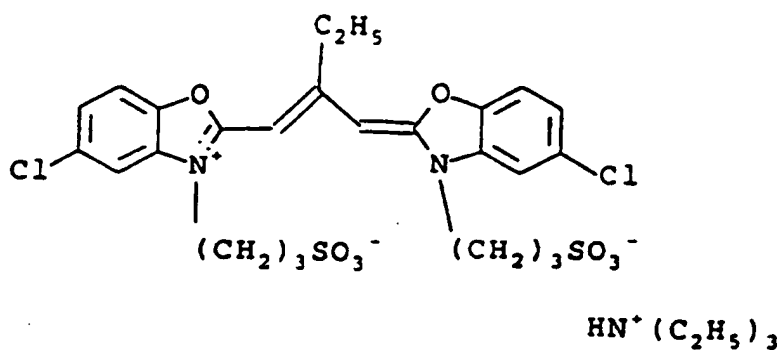
8. The process of claim 6 wherein the dye has the structure



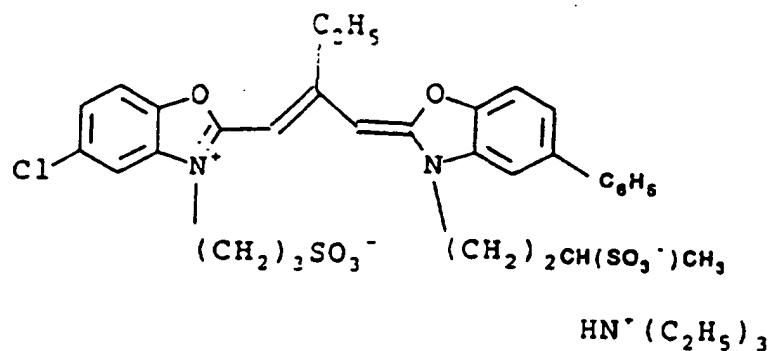
9. The process of claim 6 wherein the dye has the structure



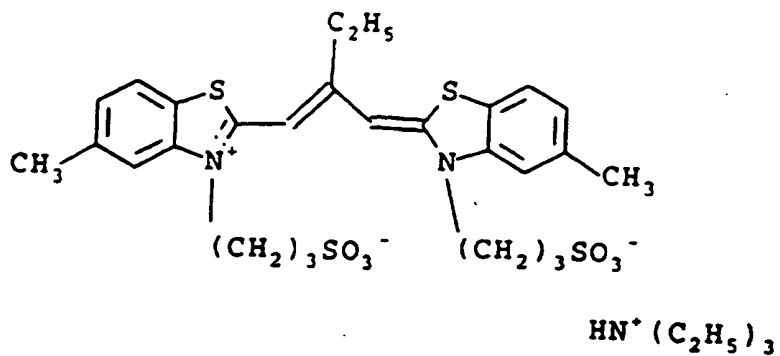
10. The process of claim 6 wherein the dye has the structure



11. The process of claim 6 wherein the dye has the structure

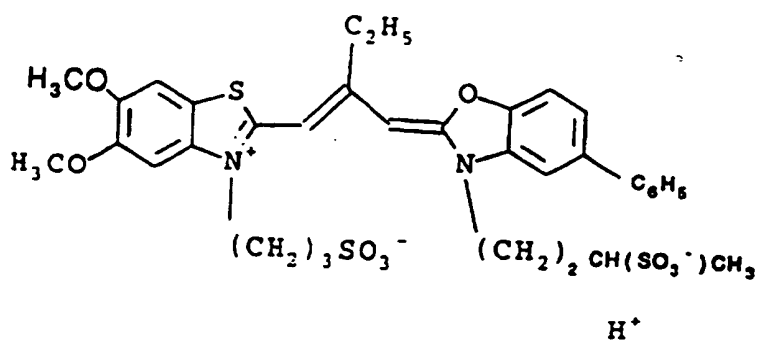


12. The process of claim 6 wherein the dye has the structure



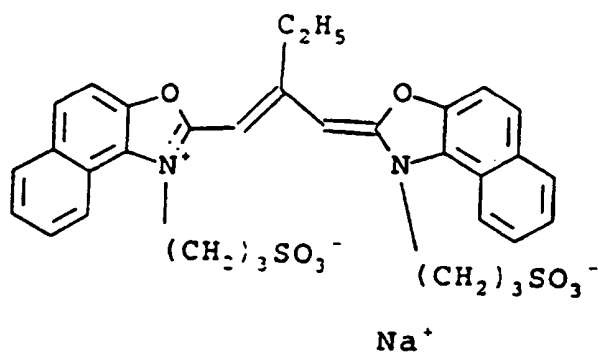
VI

13. The process of claim 6 wherein the dye has the structure



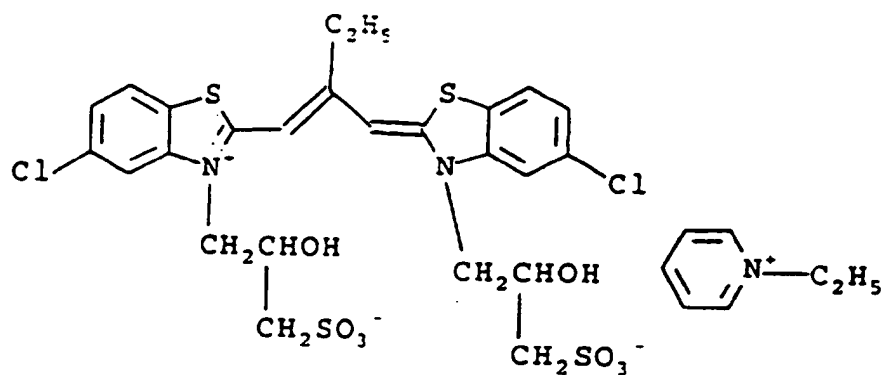
VII

14. The process of claim 6 wherein the dye has the structure



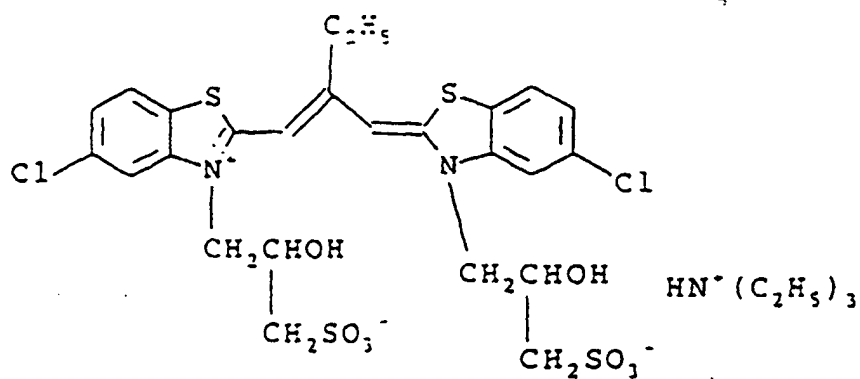
VIII

15. The process of claim 6 wherein the dye has the structure



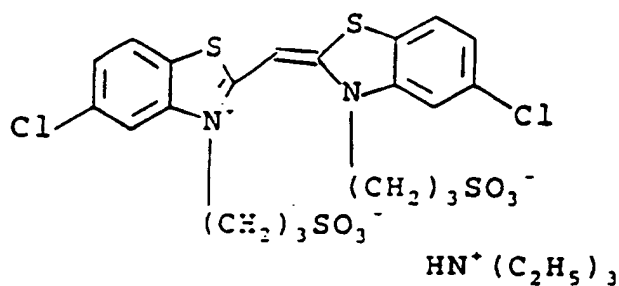
IX

16. The process of claim 6 wherein the dye has the structure



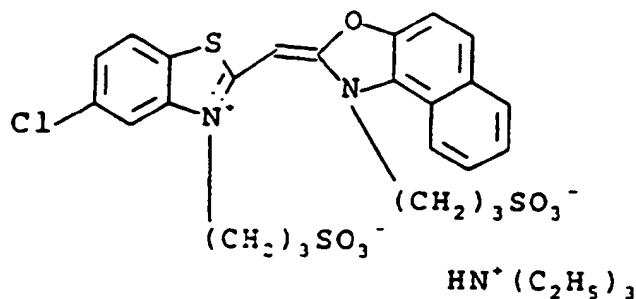
X

17. The process of claim 6 wherein the dye has the structure



XI

18. The process of claim 6 wherein the dye has the structure

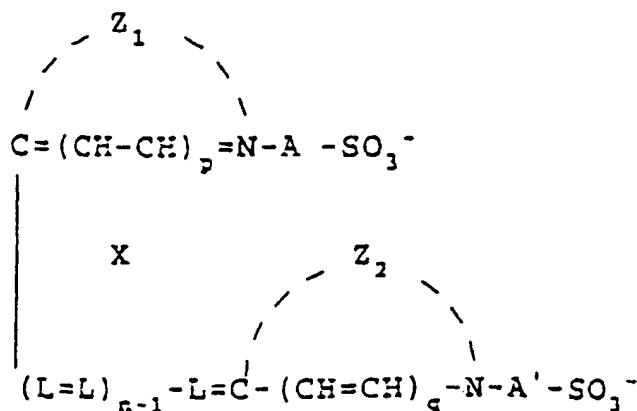


19. The process of any one of claims 1 to 18 wherein the dye is a powder capable of passing through a 1 mm sieve.

20. The process of any one of claims 1 to 19 wherein the dye is added to a water-polymer medium containing gelatin.

Patentansprüche

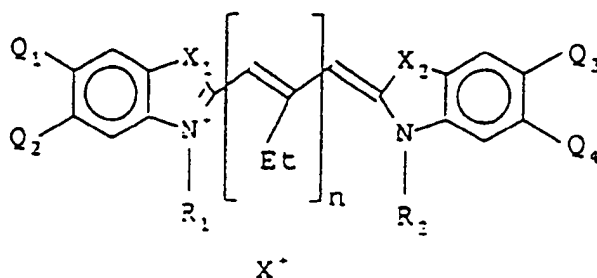
1. Verfahren zur Herstellung von konzentrierten Farbstoff-Wasser-Zusammensetzungen für die spektrale Sensibilisierung photographischer Emulsionen in Abwesenheit eines Lösungsmittels oder oberflächenaktiven Mittels, das umfaßt die Zugabe eines Sensibilisierungsfarbstoffes mit einer Löslichkeit in Wasser von mindestens 0,005 Gew.-% zu Wasser oder einem Wasser-Polymer-Medium unter Bewegung bei einer Temperatur von 20 bis 50°C bei einer Konzentration des Farbstoffes, die die Menge übersteigt, die in dem Wasser oder dem Wasser-Polymer-Medium bei den Herstellungs-, Verwendungs- oder Aufbewahrungstemperaturen löslich ist, und Fortsetzung der Bewegung mindestens 30 Minuten lang, vorzugsweise bis zu 5 Stunden.
2. Verfahren nach Anspruch 1, bei dem 0,5 bis 5 Gew.-% des Farbstoffes, bezogen auf das Gesamtgewicht der Mischung, zu dem Wasser oder dem Wasser-Polymer-Medium zugegeben werden.
3. Verfahren nach Anspruch 2, bei dem eine Bewegung (p/kg) von größer als 50×10^9 angewandt wird.
4. Verfahren nach Anspruch 2 oder 3, bei dem der Farbstoff ein spektral sensibilisierender Cyaninfarbstoff ist.
5. Verfahren nach Anspruch 4, bei dem der Cyaninfarbstoff der Formel entspricht:



worin Z_1 und Z_2 jeweils unabhängig voneinander die Atome darstellen, die zur Vervollständigung eines substituierten oder unsubstituierten heterocyclischen Kernes erforderlich sind, worin L unabhängig voneinander steht für

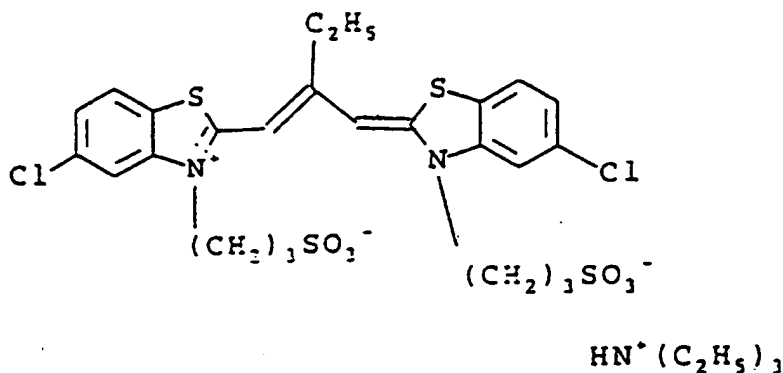
eine substituierte oder unsubstituierte Methingruppe, worin n eine positive Zahl von 1 bis 4 ist, worin p und q jeweils unabhängig voneinander stehen für 0 oder 1, worin X ein Kation darstellt, das zum Ausgleich der Ladung des Moleküls erforderlich ist, und worin A und A' jeweils unabhängig voneinander eine divalente verbindende Alkyl- oder substituierte Alkylgruppe darstellen.

6. Verfahren nach Anspruch 5, in dem der Farbstoff der Formel entspricht:

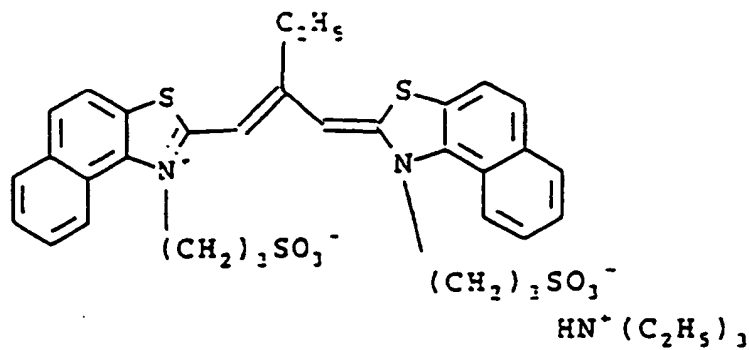


worin n für 0 oder 1 steht; X_1 und X_2 jeweils unabhängig voneinander für Sauerstoff oder Schwefel stehen; Q_1 , Q_2 , Q_3 und Q_4 jeweils unabhängig voneinander stehen für Halogen, Alkyl, Alkoxy oder die Atome enthalten können, die zur Bildung eines beta- oder linear-Naphtho-kondensierten Ringes erforderlich sind; worin R_1 und R_2 jeweils unabhängig voneinander eine Sulfoalkyl- oder substituierte Sulfoalkylgruppe darstellen; und worin X^+ ein Kation ist, wie Natrium, Wasserstoff, Triethylammonium oder Ethylpyridinium.

7. Verfahren nach Anspruch 6, in dem der Farbstoff die Struktur hat:

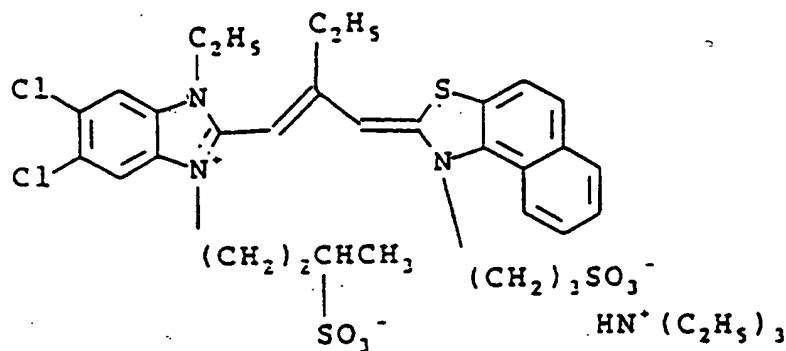


8. Verfahren nach Anspruch 6, in dem der Farbstoff die Struktur hat:



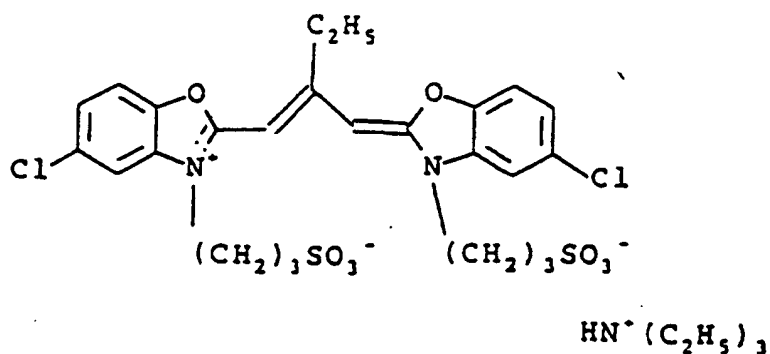
II

9. Verfahren nach Anspruch 6, in dem der Farbstoff die Struktur hat:



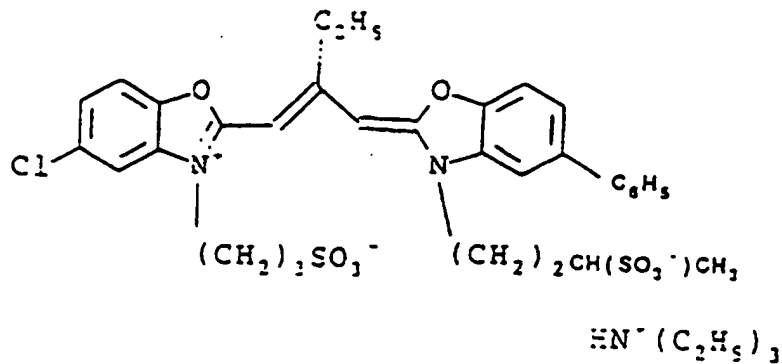
III

10. Verfahren nach Anspruch 6, in dem der Farbstoff die Struktur hat:



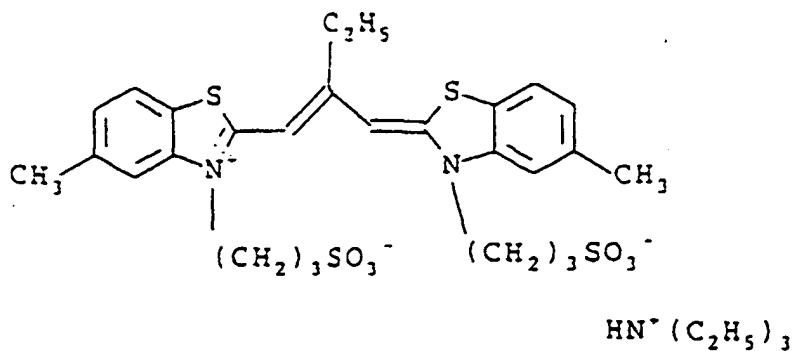
IV

11. Verfahren nach Anspruch 6, in dem der Farbstoff die Struktur hat:



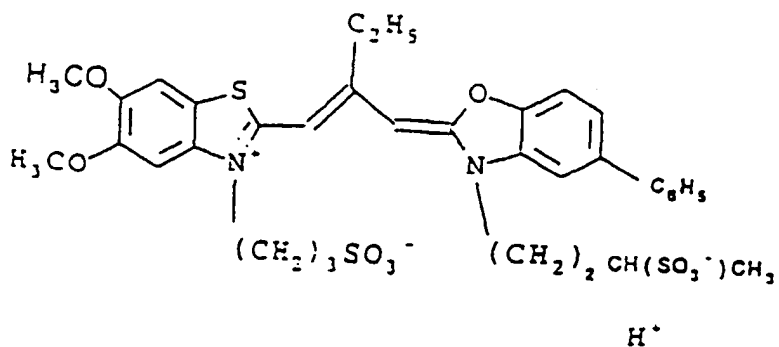
V

12. Verfahren nach Anspruch 6, in dem der Farbstoff die Struktur hat:



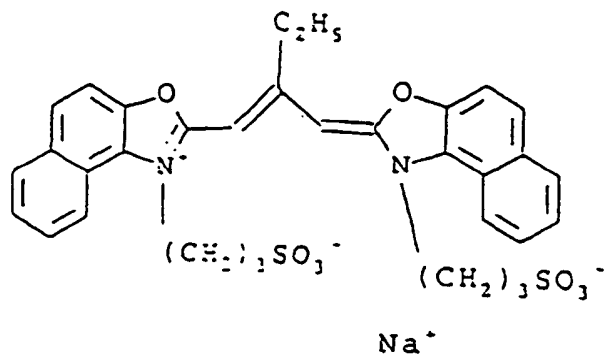
VI

13. Verfahren nach Anspruch 6, in dem der Farbstoff die Struktur hat:

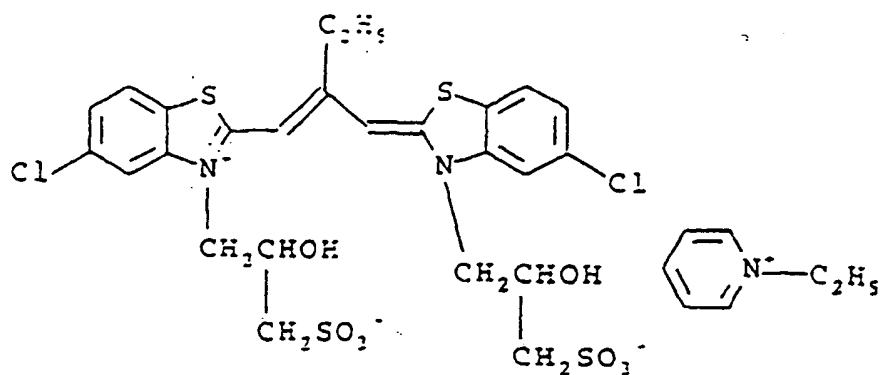


VII

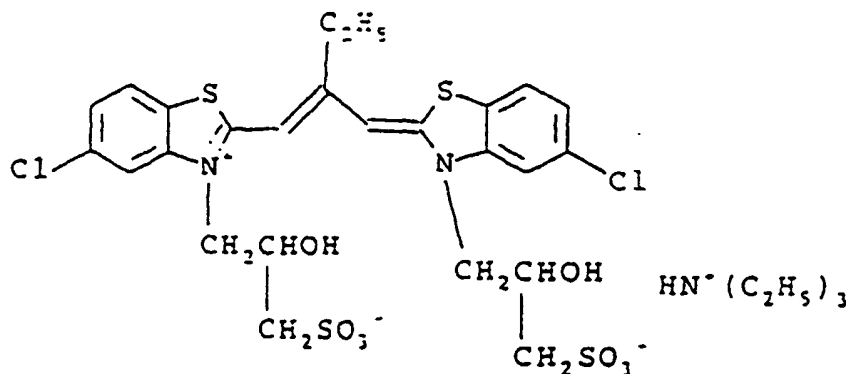
14. Verfahren nach Anspruch 6, in dem der Farbstoff die Struktur hat:



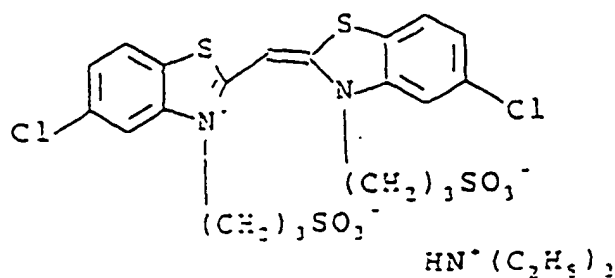
15. Verfahren nach Anspruch 6, in dem der Farbstoff die Struktur hat:



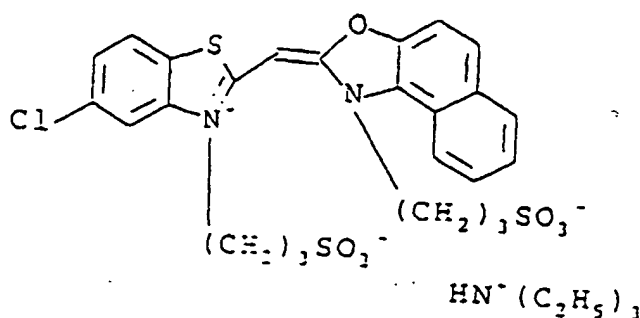
16. Verfahren nach Anspruch 6, in dem der Farbstoff die Struktur hat:



17. Verfahren nach Anspruch 6, in dem der Farbstoff die Struktur hat:



15 18. Verfahren nach Anspruch 6, in dem der Farbstoff die Struktur hat:

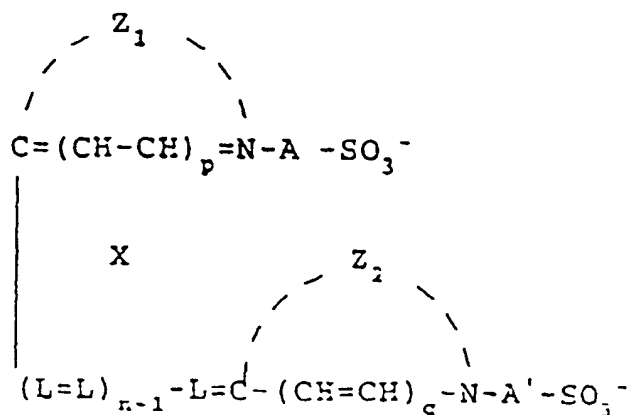


35 19. Verfahren nach einem der Ansprüche 1 bis 18, in dem der Farbstoff ein Pulver ist, das durch ein Sieb von 1 mm hindurchzutreten vermag.

40 20. Verfahren nach einem der Ansprüche 1 bis 19, in dem der Farbstoff einem Wasser-Polymer-Medium zugegeben wird, das Gelatine enthält.

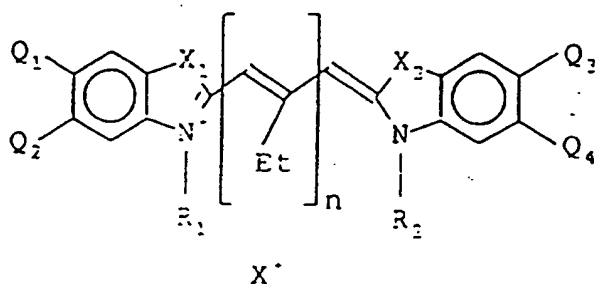
40 Revendications

- 45 1. Procédé pour préparer des compositions aqueuses concentrées de colorant pour sensibiliser spectralement des émulsions photographiques en l'absence de solvant ou d'agent tensio-actif, qui comprend l'addition à l'eau ou à un milieu polymère aqueux d'un colorant sensibilisateur ayant une solubilité dans l'eau d'au moins 0,005 pourcent en poids, en agitant à une température comprise entre 20 et 50 °C, à une concentration de colorant qui dépasse la quantité de colorant soluble dans l'eau ou le milieu polymère aqueux aux températures de préparation, d'utilisation ou de stockage, et la poursuite de l'agitation pendant une période d'au moins 30 minutes et de préférence allant jusqu'à 5 heures.
- 50 2. Procédé selon la revendication 1, dans lequel 0,5 à 5 pourcent en poids de colorant, par rapport au poids total du mélange, sont ajoutés à l'eau ou à un milieu polymère aqueux.
3. Procédé selon la revendication 2, dans lequel une agitation (p/kg) supérieure à 50×10^9 est effectuée.
- 55 4. Procédé selon la revendication 2 ou 3, dans lequel le colorant est un colorant sensibilisateur spectral cyanine.
5. Procédé selon la revendication 4, dans lequel le colorant cyanine répond à la formule :



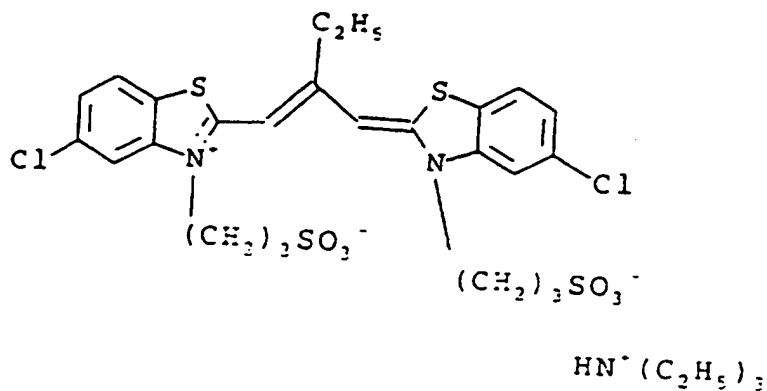
où Z_1 et Z_2 représentent chacun séparément les atomes nécessaires pour compléter un hétérocycle substitué ou non, chaque L représente individuellement un groupe méthinique substitué ou non, n est un nombre entier positif compris entre 1 et 4, p et q représentent chacun séparément 0 ou 1, X représente un cation requis pour équilibrer la charge de la molécule, et A et A' représentent chacun séparément un groupe de liaison divalent alkyle ou alkyle substitué.

6. Procédé selon la revendication 5, dans lequel le colorant répond à la formule :

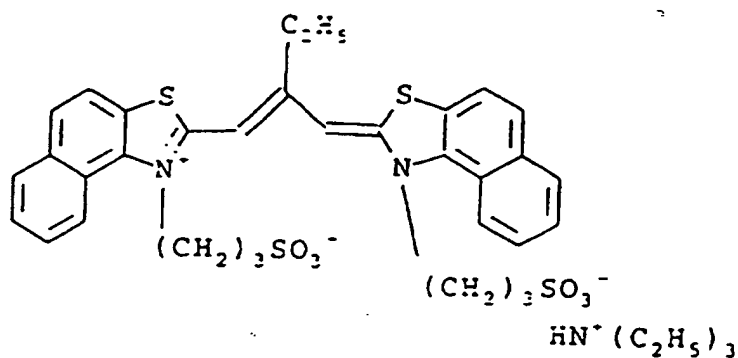


où n est égal à 0 ou 1 ; X_1 et X_2 représentent chacun séparément un oxygène ou un soufre ; Q_1 , Q_2 , Q_3 et Q_4 représentent chacun séparément un halogène, un groupe alkyle ou un groupe alkoxy ou peuvent contenir les atomes nécessaires pour former un noyau condensé naphto bêta ou linéaire ; R_1 et R_2 représentent chacun séparément un groupe sulfoalkyle ou sulfoalkyle substitué ; et X^+ est un cation tel que le sodium, l'hydrogène, le triéthylammonium ou l'éthylpyridinium.

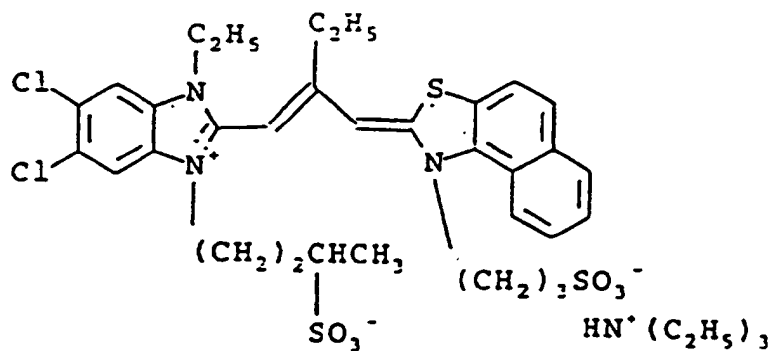
7. Procédé selon la revendication 6, dans lequel le colorant a la structure :



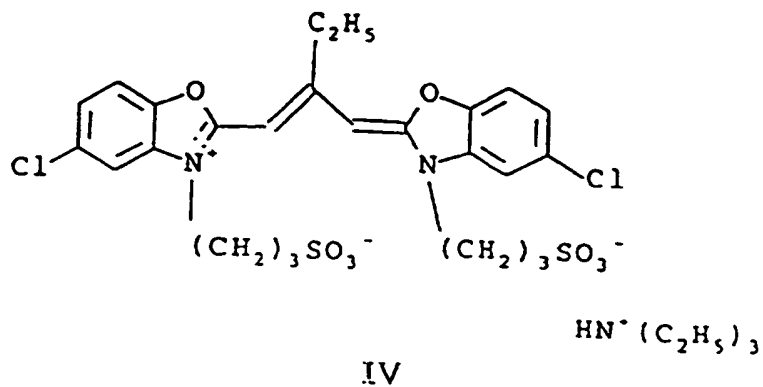
8. Procédé selon la revendication 6, dans lequel le colorant a la structure :



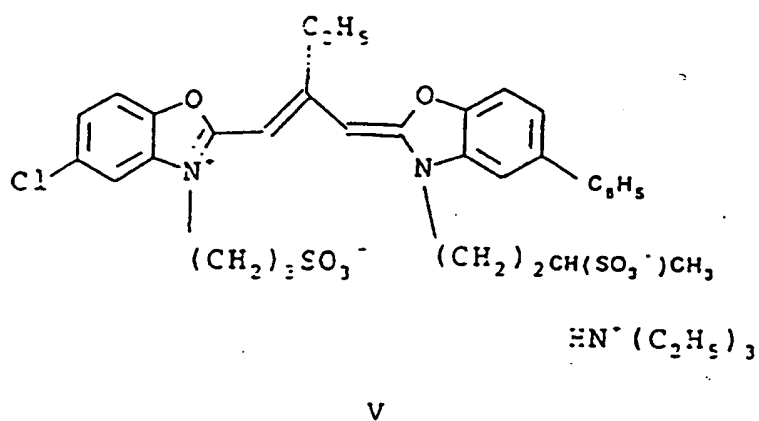
9. Procédé selon la revendication 6, dans lequel le colorant a la structure :



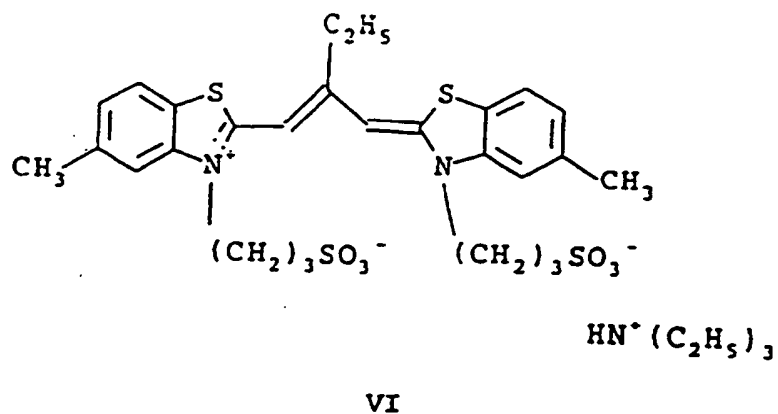
10. Procédé selon la revendication 6, dans lequel le colorant a la structure :



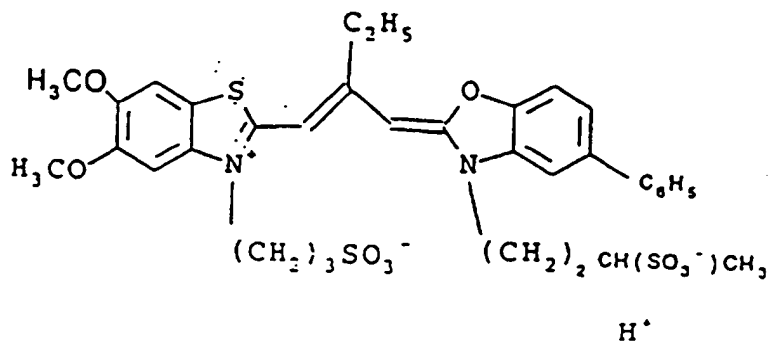
11. Procédé selon la revendication 6, dans lequel le colorant a la structure :



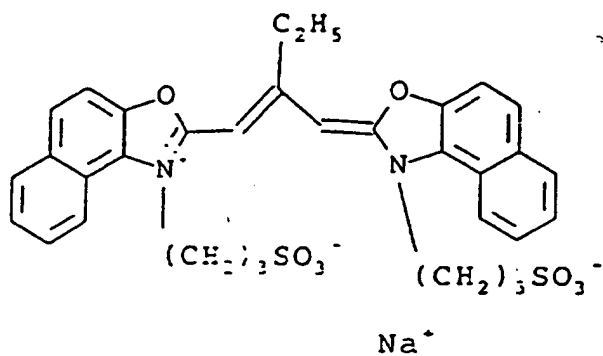
12. Procédé selon la revendication 6, dans lequel le colorant a la structure :



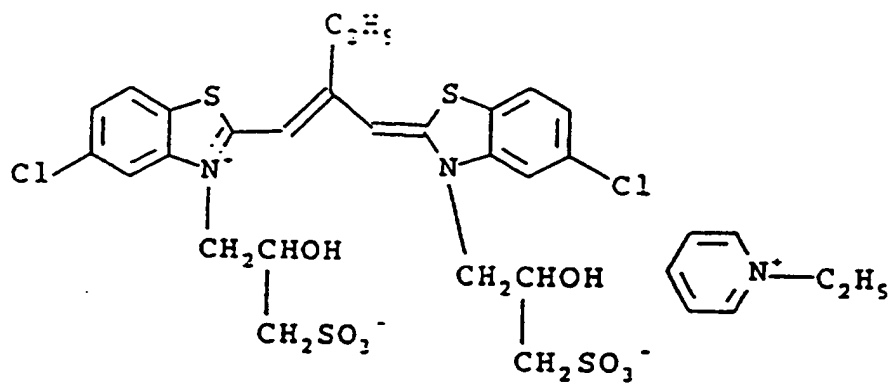
13. Procédé selon la revendication 6, dans lequel le colorant a la structure :



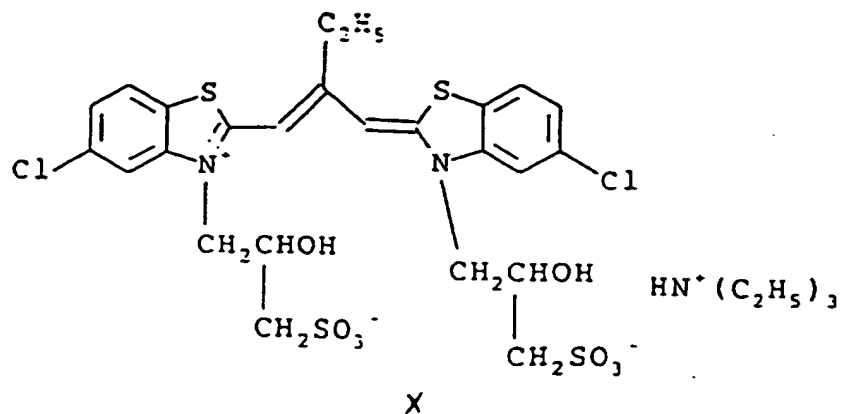
14. Procédé selon la revendication 6, dans lequel le colorant a la structure :



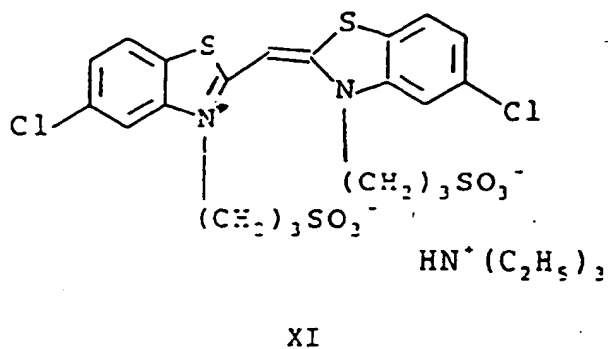
15. Procédé selon la revendication 6, dans lequel le colorant a la structure :



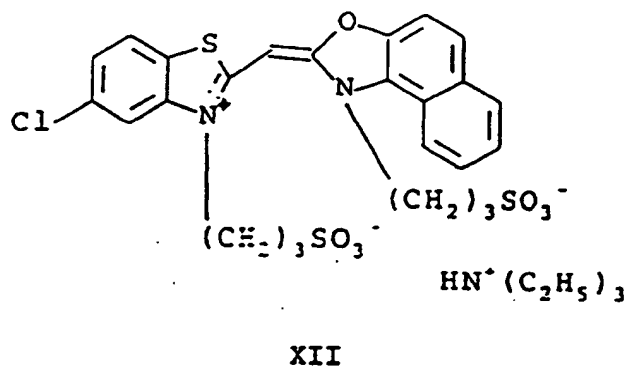
16. Procédé selon la revendication 6, dans lequel le colorant a la structure :



17. Procédé selon la revendication 6, dans lequel le colorant a la structure :



18. Procédé selon la revendication 6, dans lequel le colorant a la structure :



19. Procédé selon l'une quelconque des revendications 1 à 18, dans lequel le colorant est une poudre capable de traverser un tamis de 1 mm de maillage.

20. Procédé selon l'une quelconque des revendications 1 à 19, dans lequel le colorant est ajouté à un milieu polymère aqueux contenant de la gélatine.